National Aeronautics and Space Administration

What's on the Surface? Physics and Chemistry of Delta-doped Surfaces

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Next Generation UV Instrument Technologies Enabling Missions in Astrophysics, Cosmology and Planetary Sciences

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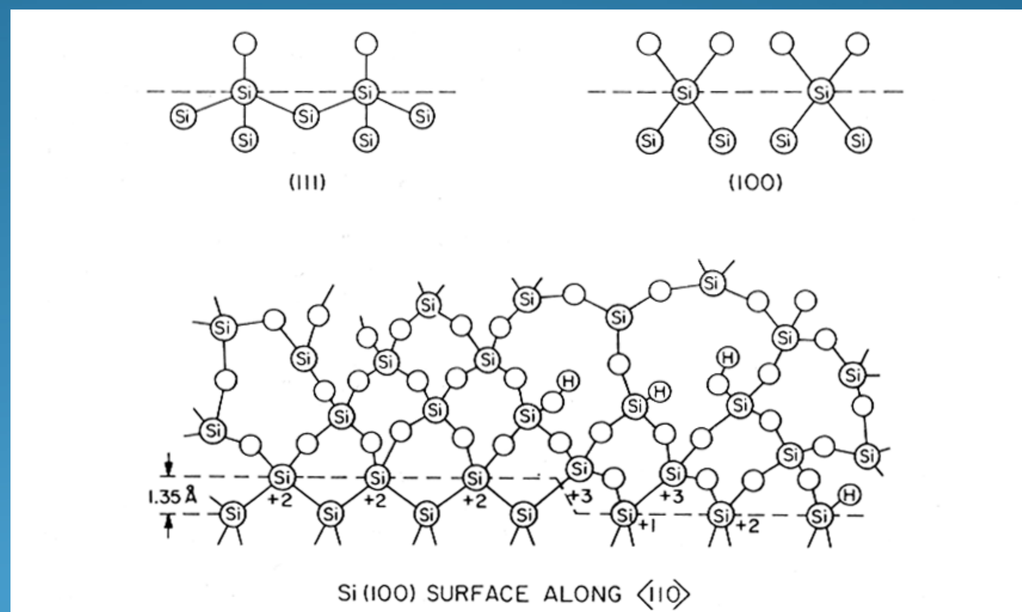
Outline

1. Detector surfaces and the problem of stability
2. Delta-doped detectors
3. Physics of Delta-doped Silicon
4. Chemistry of the Si-SiO_2 Interface
5. Physics and Chemistry of Delta-doped Surfaces
    1. Compensation
    2. Inversion
    3. Quantum exclusion

Nanostructured Silicon for Surface Passivation

"The surface, being the boundary between two phases, is at the same time the boundary between two sciences: physics and chemistry."
-- F. F. Vol'kenshtein, 1967



"The present results clarify the importance of controlling interface structure on the atomic scale."

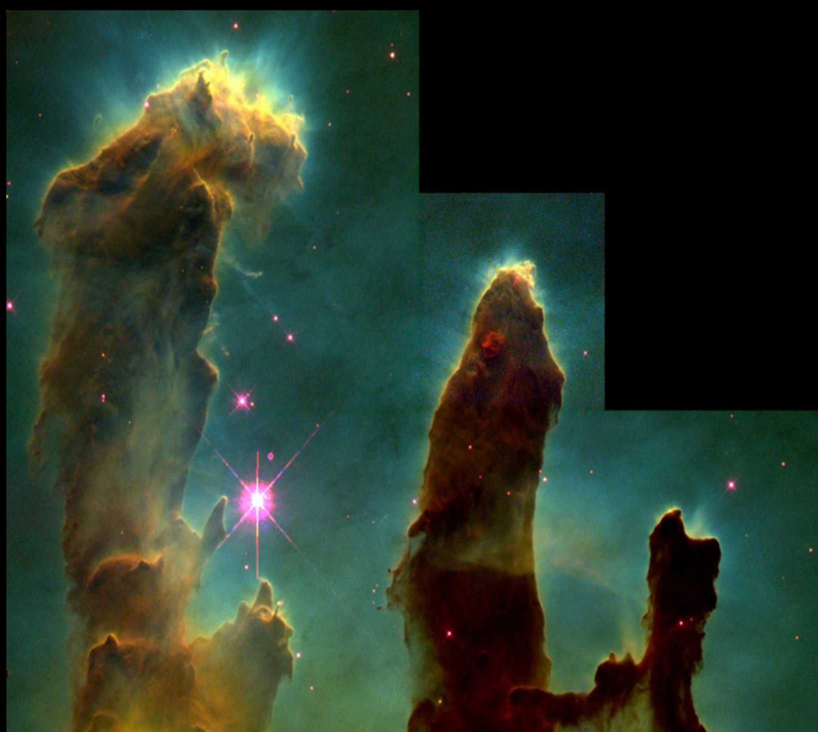
—Y. Gohda, S. Watanabe, and A. Groß, 2008

Detector Surfaces and the Problem of Stability

A Revolution in Imaging

"CCDs were born in the Si-SiO_2 revolution and created their own revolution in widespread imaging device applications."

-- George Smith, co-inventor of CCDs and Nobel Laureate

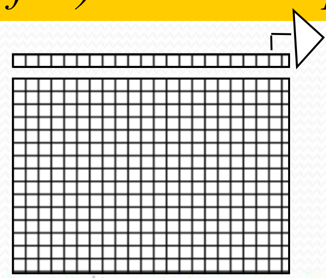


George E. Smith, "The invention and early history of the CCD," Nuclear Instruments and Methods in Physics Research A, 607: 1-6, 2009.

Silicon Imager Architectures: CCD vs. CMOS

Charge-coupled Device (CCD)
Serial readout device with charge transfer and one (or few) readout amplifiers.

CMOS Imaging Array
Parallel readout with few charge transfers and one readout amplifier per pixel.



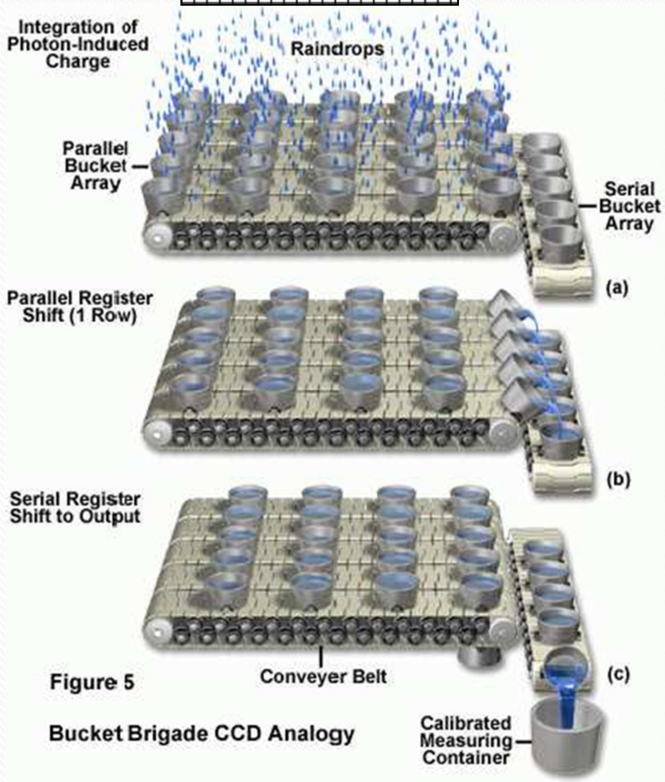
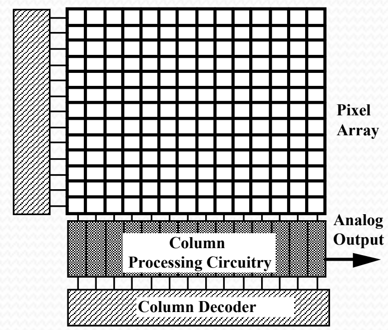
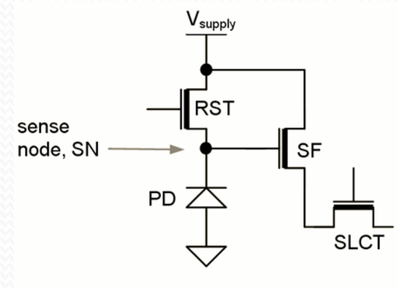


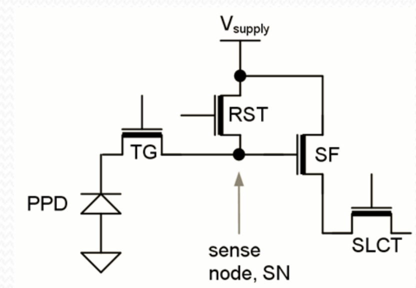
Figure 5
Bucket Brigade CCD Analogy



CMOS APS



(a) 3T pixel

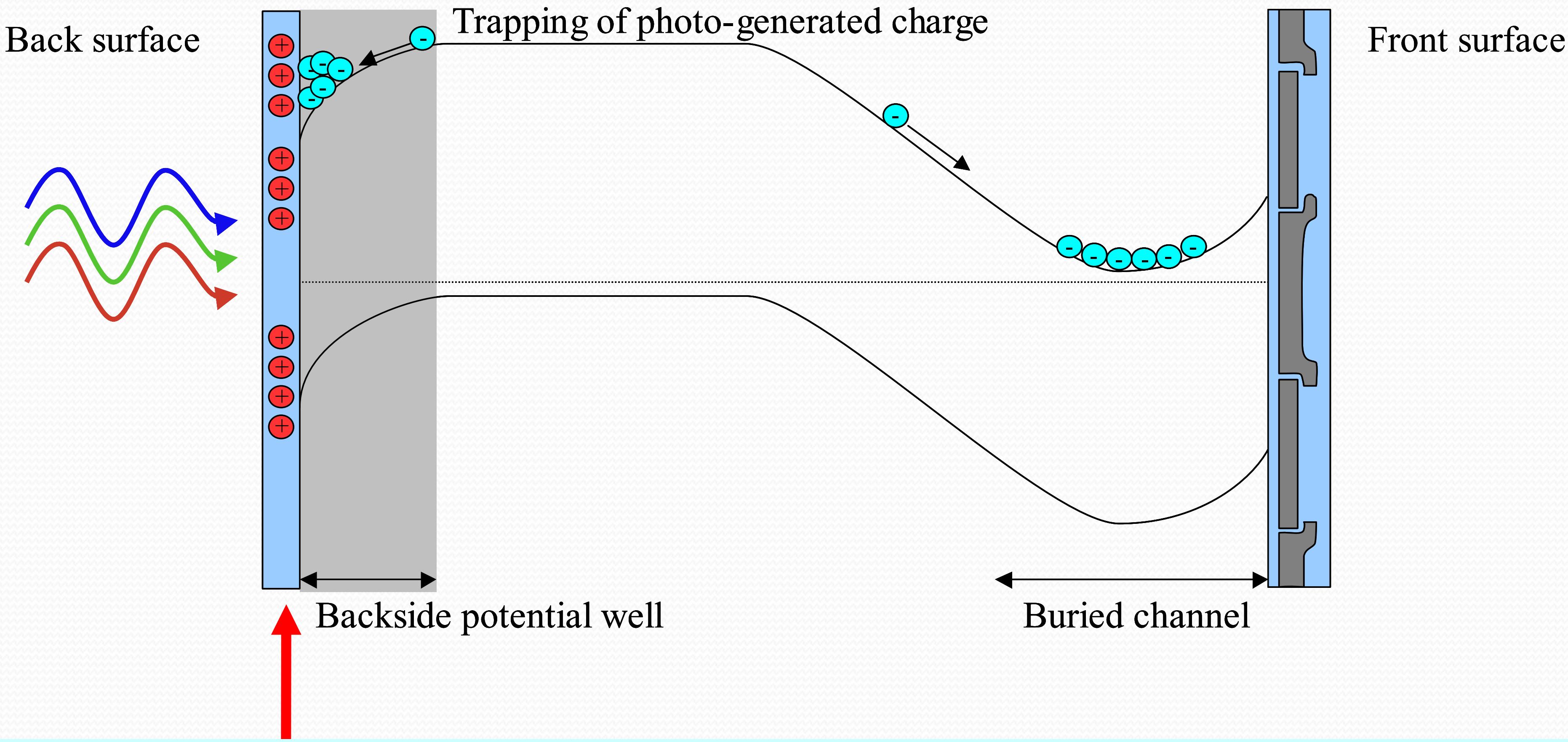


(b) 4T pinned photodiode pixel

Scientific CMOS imagers are catching up with CCDs
– Jim Janesick, 2009

UV Astronomy and the Surface Problem

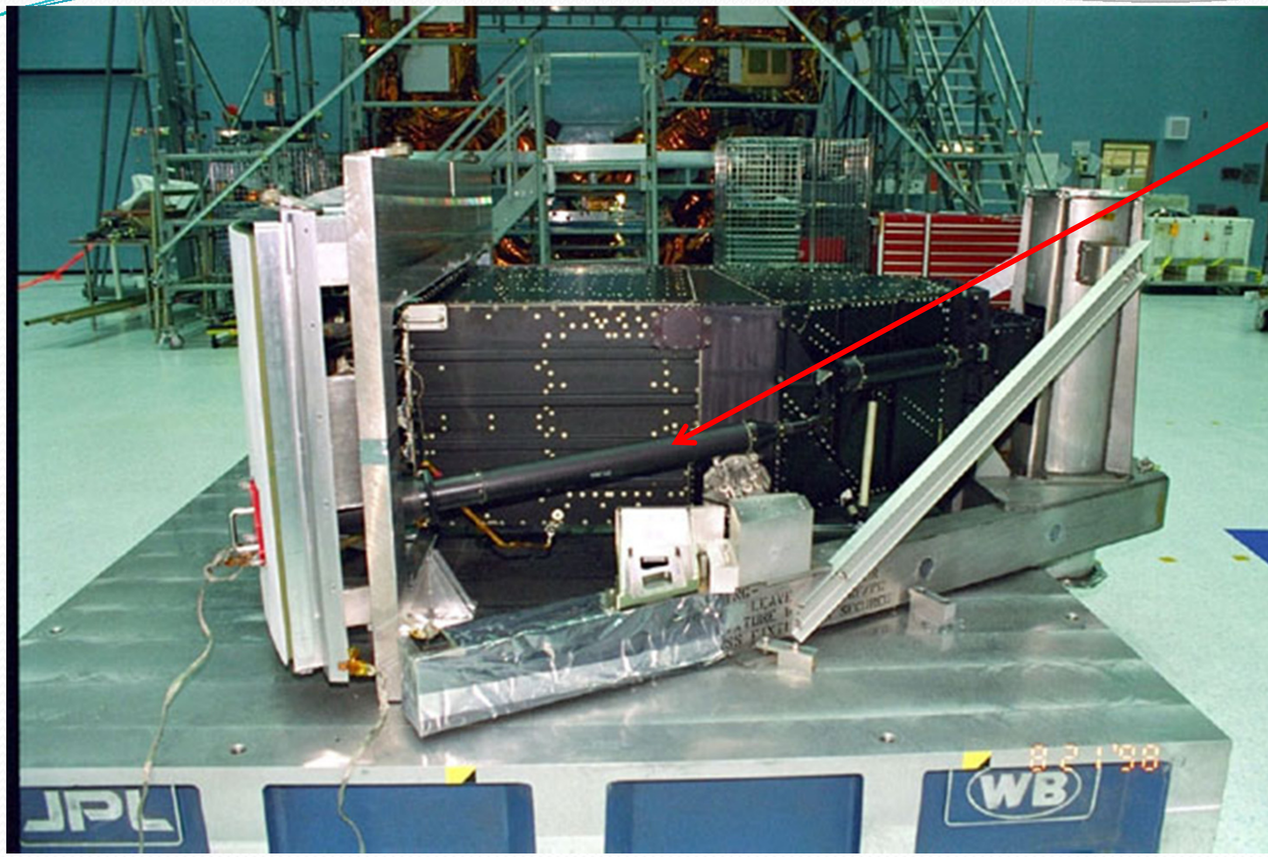
In 1984, ***quantum efficiency hysteresis*** was discovered during thermal vacuum testing of Wide Field Camera (WFPC-1).



<u>Quantum efficiency hysteresis</u> – CCD response depends on prior illumination history

- Unacceptable – Hubble needs stability to 1% over 30 days…
- Passivation of surface defects is necessary to solve the problem.

Quantum Efficiency Hysteresis on Hubble



Light pipe added to WF/PC instrument to expose detectors to UV from sunlight

WF/PC1 (1983-1992) Massive UV flood at 250 nm through light pipe

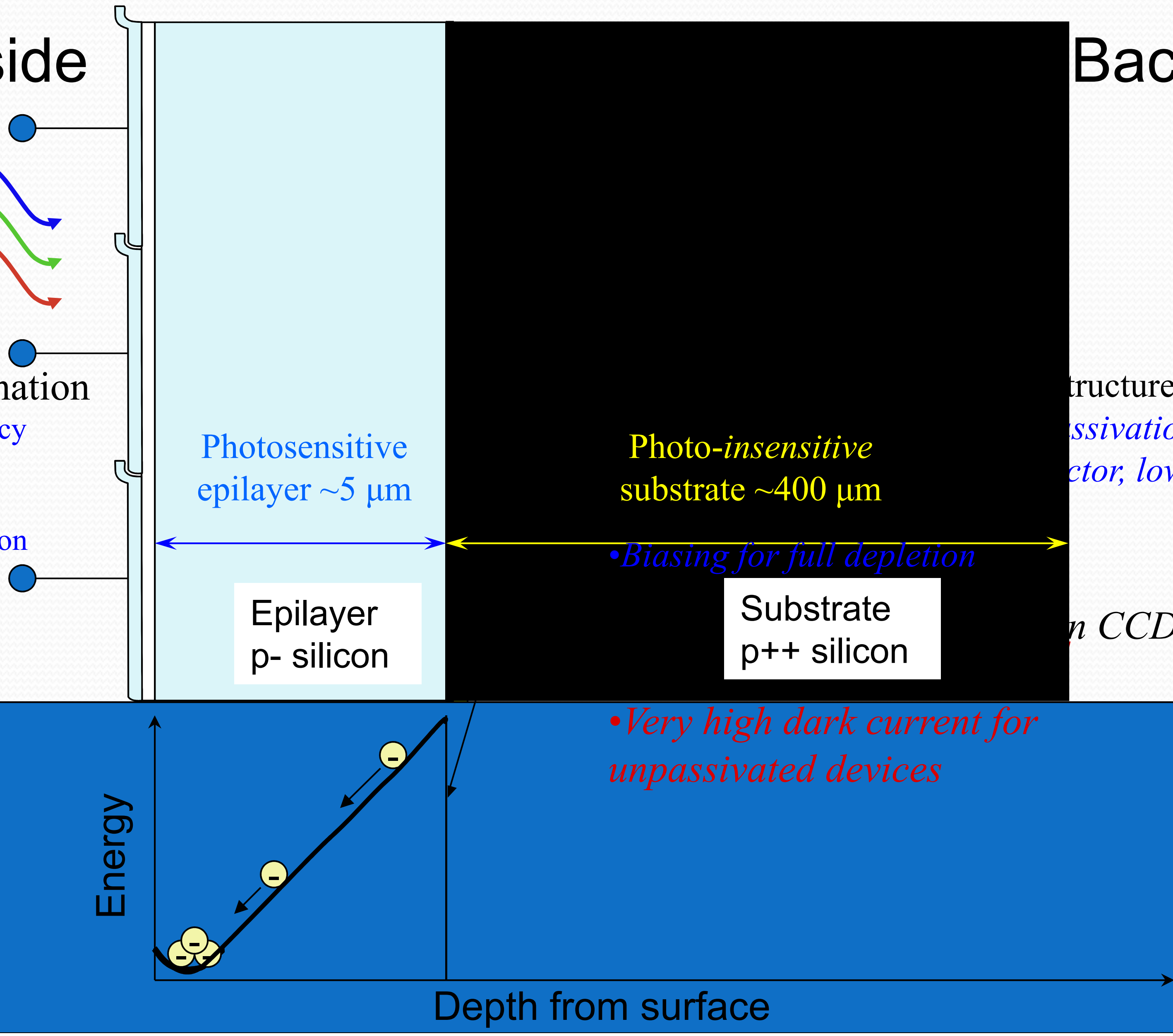
WF/PC2 (1983-1992) Flash gate, biased flash gate

WF/PC2 (1992-2009) Front illuminated Loral CCDs with lumogen

WFC3 (2009-present) Back illuminated, ion-implanted CCDs

John T. Trauger, "Sensors for the Hubble Space Telescope Wide Field and Planetary Cameras (1 and 2)," in *CCDs in astronomy: Proceedings of the Conference, Tucson, AZ, Sept. 6-8, 1989 (A91-45976 19-33)*, San Francisco, CA, Astronomical Society of the Pacific, 1990, p. 217-230

Detector electronic structure



Front illumination
- Low efficiency
  - Absorption
  - Fill factor
- Low resolution
  - Scattering
  - Diffraction
  - Diffusion

tructure

ssivation

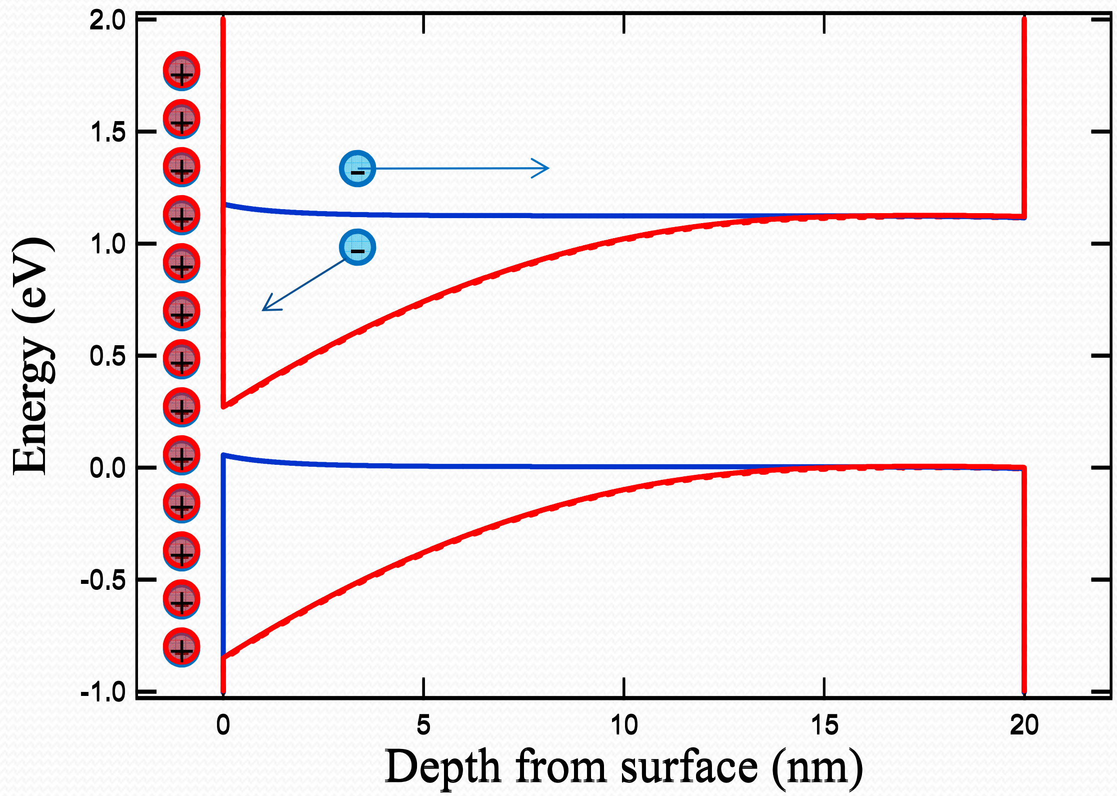
ctor, low dark current

•Biasing for full depletion

n CCDs

•Very high dark current for unpassivated devices

Quantum Efficiency Hysteresis



Negative charge → Accumulation

Positive charge → Depletion

Surface passivation: The conventional approach....

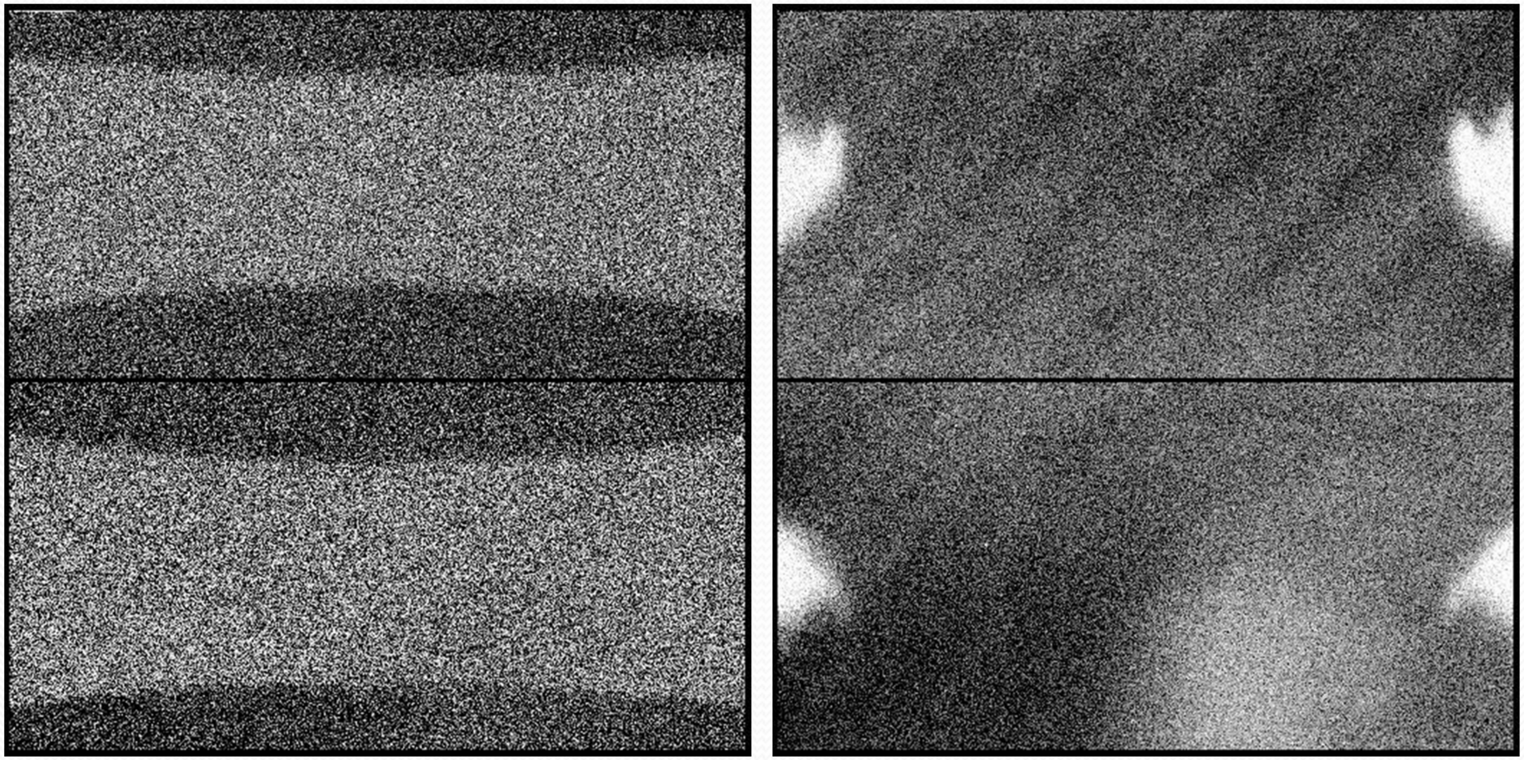
Trapped charge affects fields → quantum efficiency hysteresis

Surface passivation requires high electric field and low surface defect density

The Evolution of CCD Surfaces on Hubble

- *Surface doping – early attempts*
  - Precision thinning leaves residual p+ (early *WF/PC 1*)
- *Chemical charging – early attempts*
  - UV flood (*late WF/PC 1*)
  - Platinum flash gate (*WF/PC 2 – never flown*)
  - Biased flash gate (WF/PC 2 – never flown)
- *Phosphor coatings*
  - Front-illuminated with lumogen (*WF/PC 2*)
- *Chemisorption – later evolution*
  - Chemisorption (UA/ M. Lesser – *ACS HRC*)
- *Surface doping*
  - Ion implantation (*WFC3*)

Quantum Efficiency Hysteresis in WFC3

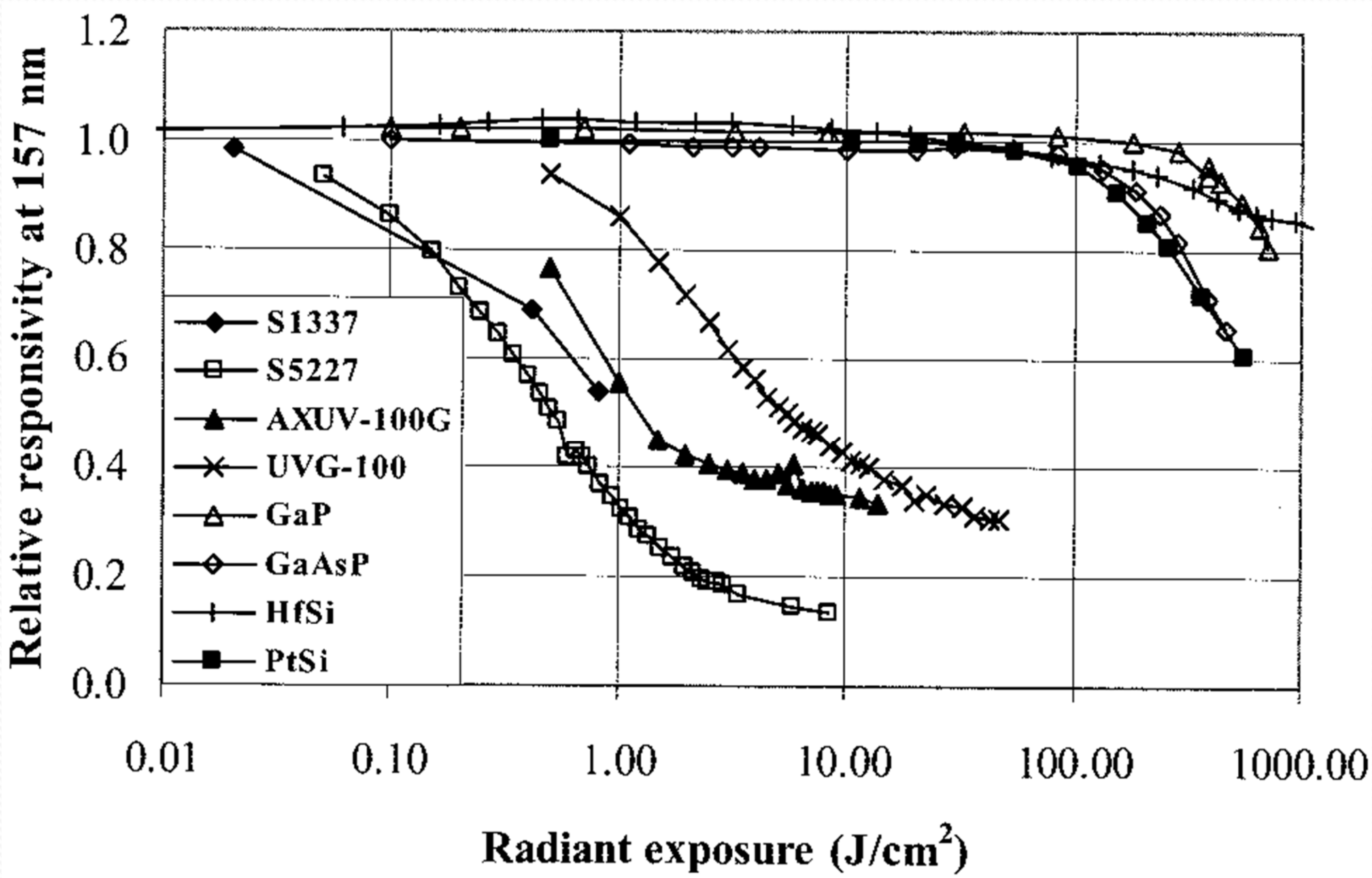


Ion-implanted CCDs on Wide Field Camera 3

- Launched in 2009
- Instabilities on the order of a few percent
- Mitigated by on-orbit flooding with visible light to fill surface traps

Collins *et al.* SPIE proceedings 7439A-10, San Diego, CA, August 2009.

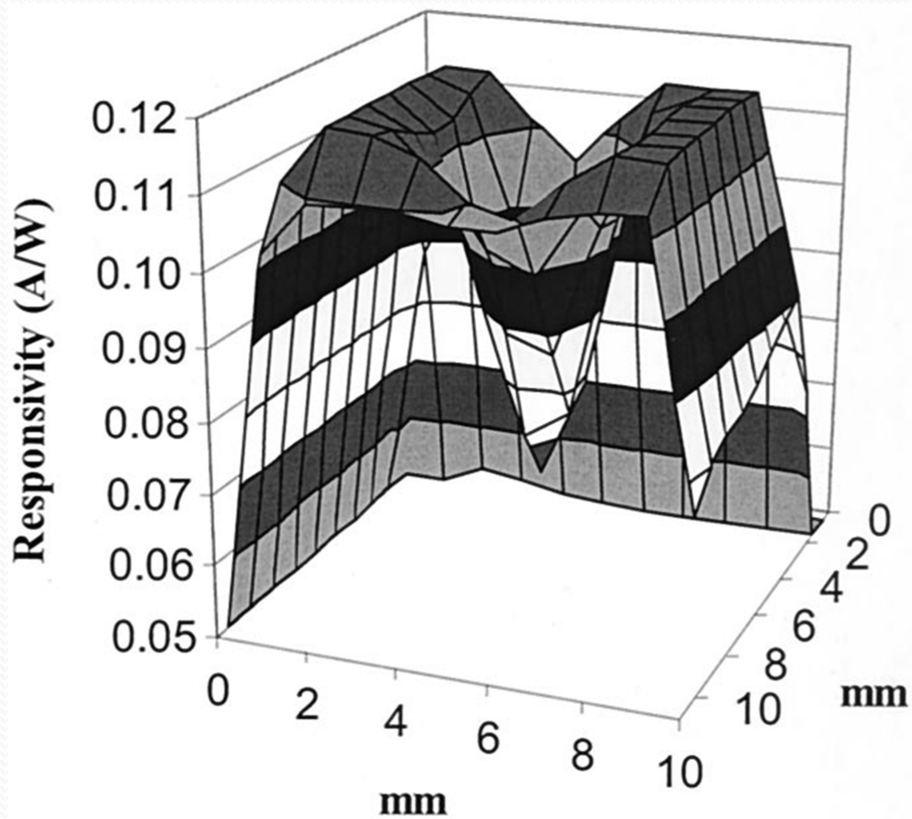
DUV Detectors and Surface Damage:
The Problem of Stability



Ping-Shine Shaw, Rajeev Gupta, Keith R. Lykke, “Stability of photodiodes under irradiation with a 157-nm pulsed excimer laser,” Applied Optics, 44(2): 197-207 (2005).

UV-induced trap formation

- Hot carrier degradation: Arp05 and Shaw05
  - SiO_2 bandgap ~8.9 eV (λ~139 nm)
  - 4.6 eV (λ~270 nm) to inject hot electrons into SiO_2 conduction band
  - 5.5 eV (λ~225 nm) to inject holes into SiO_2 valence band
  - 6.6 eV (λ~188 nm) threshold to inject electrons with enough energy to break Si-H bond and create Pb center
  - Band structure in interface region is not fully developed – hot carrier damage is possible at lower energies



Ping-Shine Shaw, Rajeev Gupta, Keith R. Lykke, "Stability of photodiodes under irradiation with a 157-nm pulsed excimer laser," Applied Optics, 44(2): 197-207 (2005).

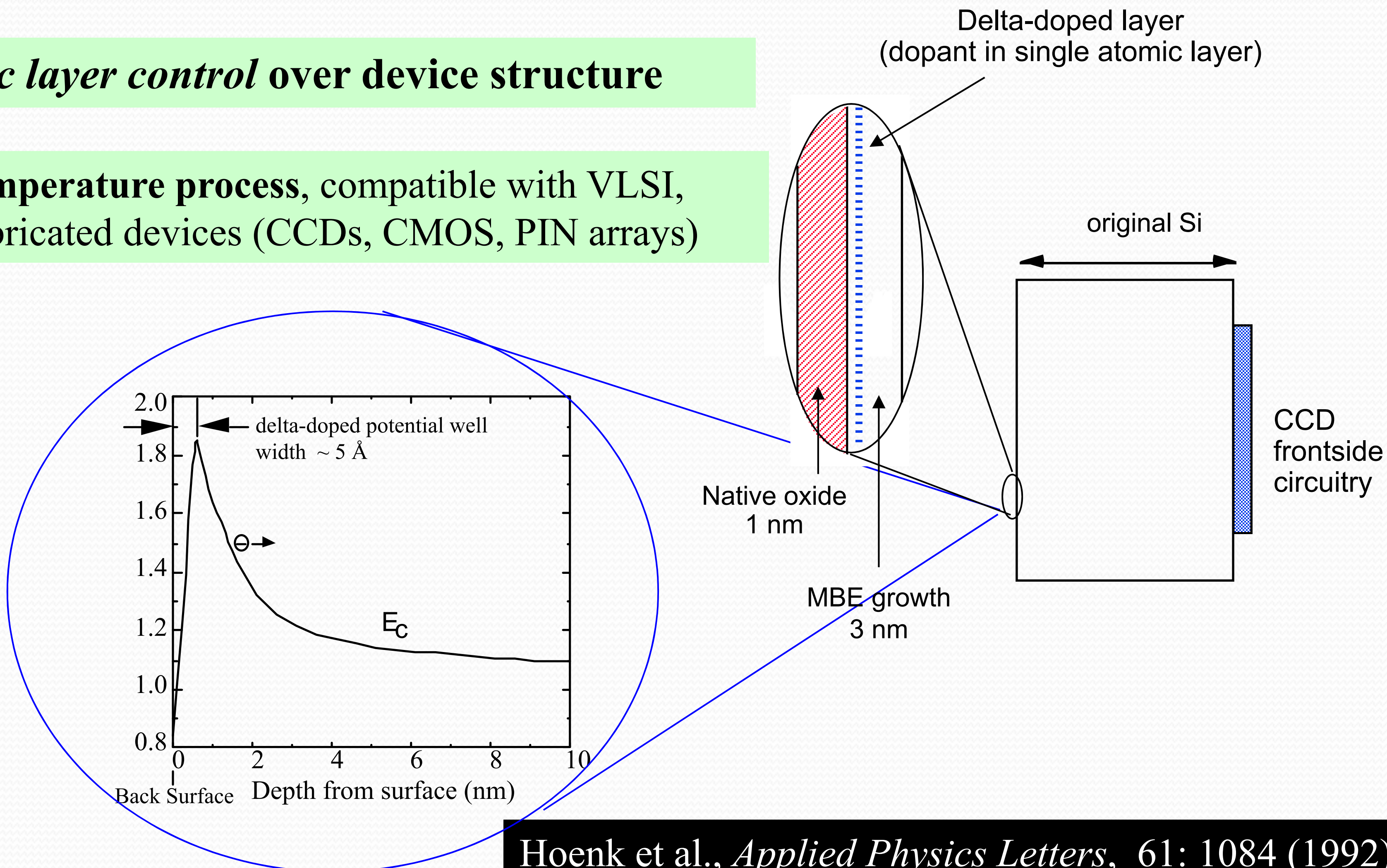
Delta-doped detectors

Nanostructured silicon for surface passivation

Delta doping for Surface Passivation

Atomic layer control **over device structure**

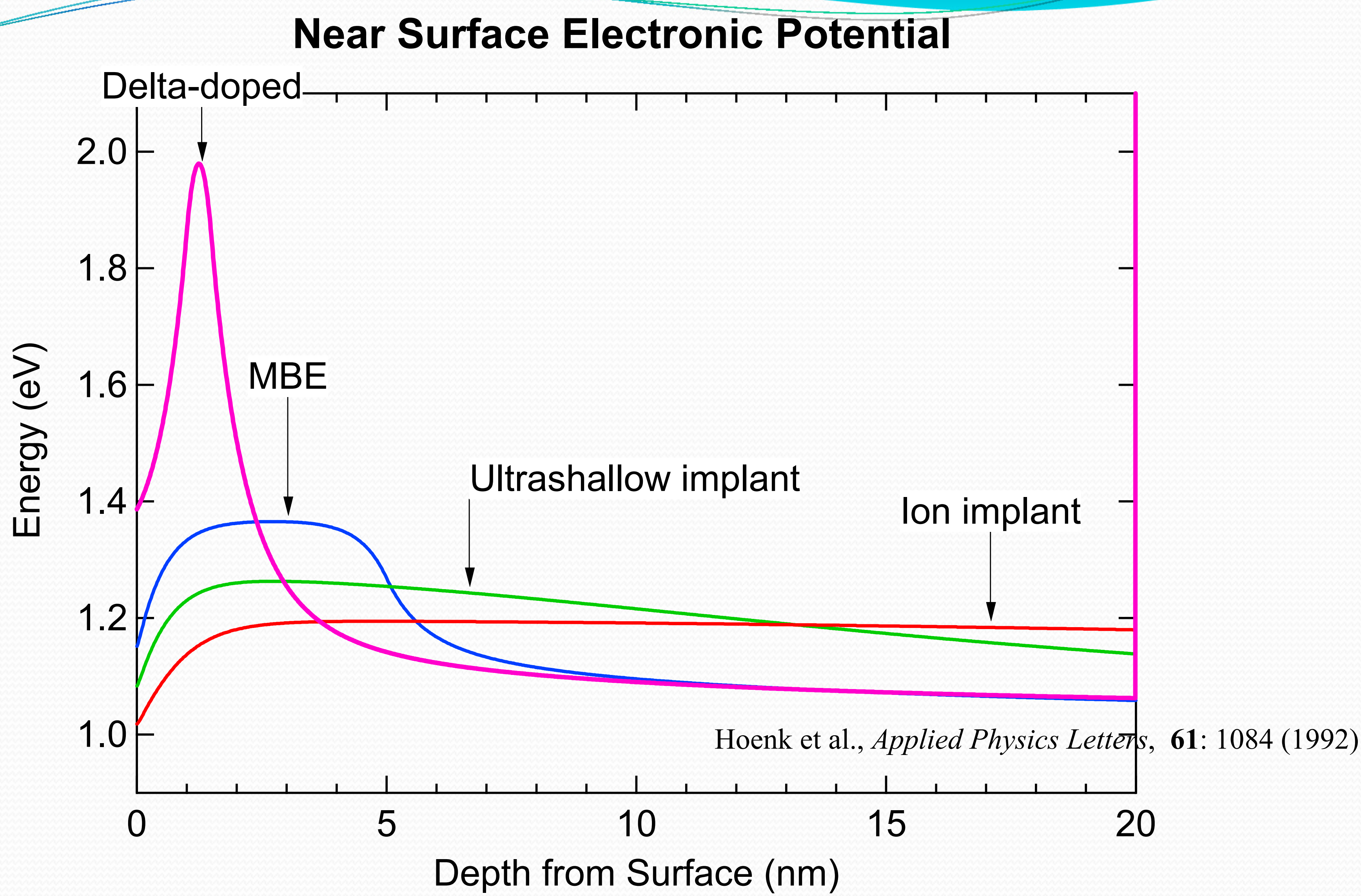
Low temperature process, compatible with VLSI, fully fabricated devices (CCDs, CMOS, PIN arrays)



Hoenk et al., *Applied Physics Letters*, 61: 1084 (1992)

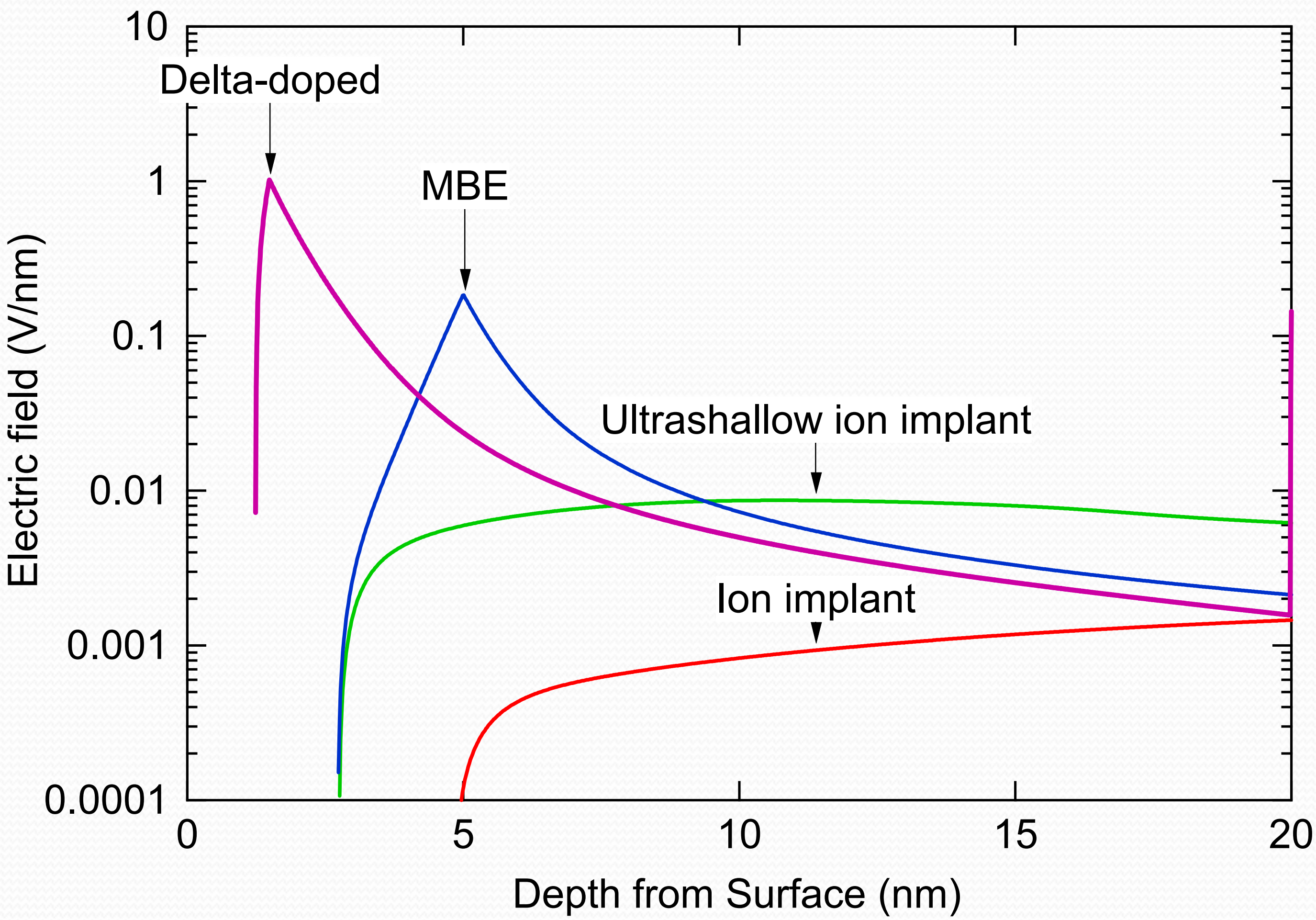
Fully-processed devices are modified using Molecular Beam Epitaxy (MBE)

Delta-doping vs. Ion implantation

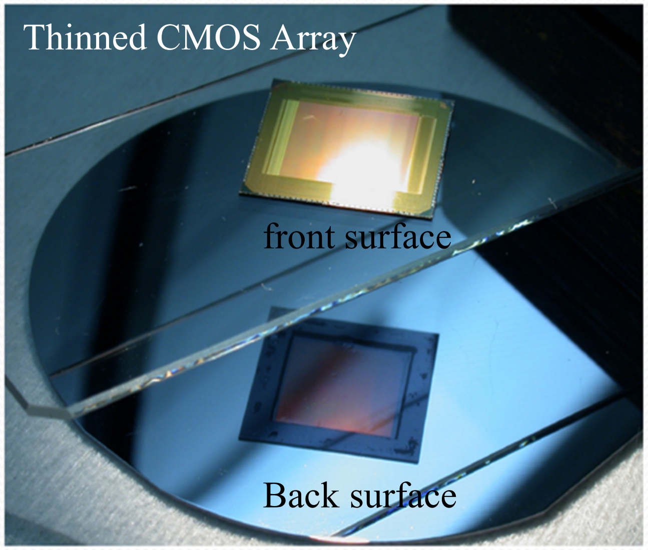


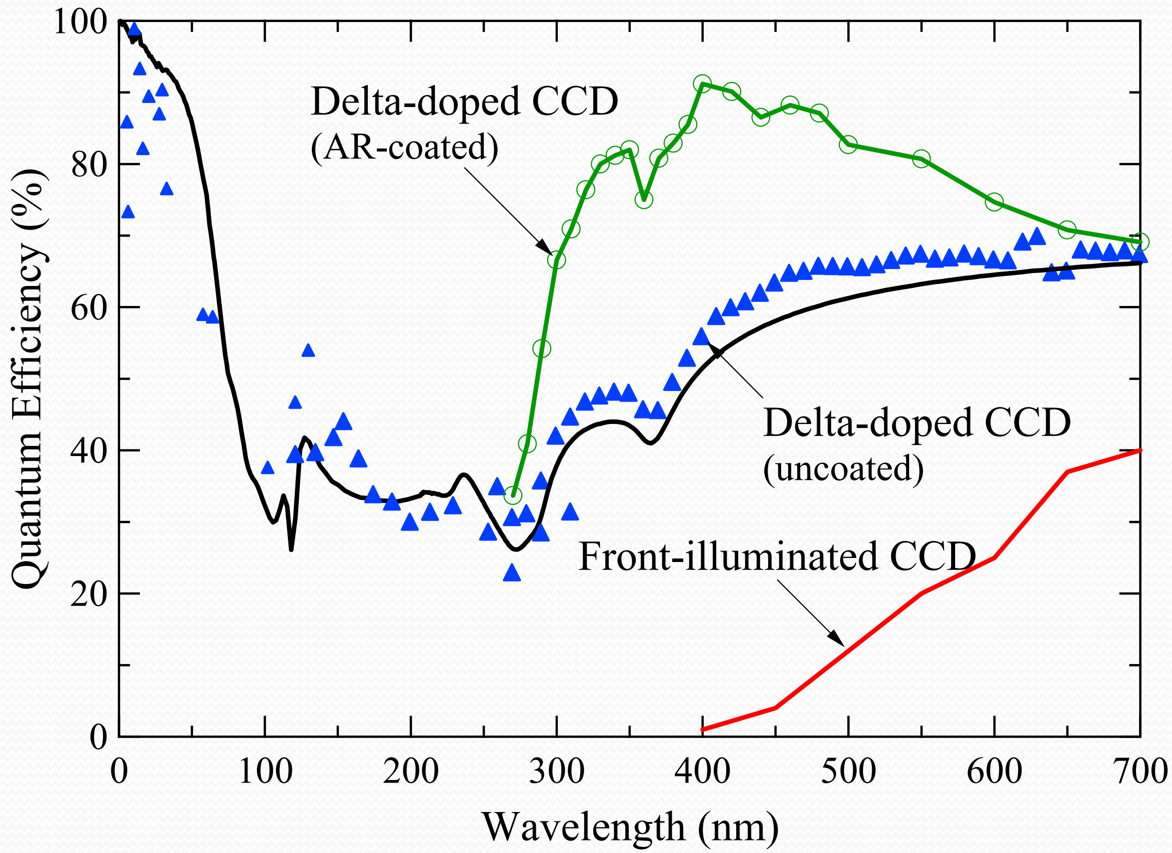
Delta doping produces highest surface electric fields of any passivation technology

Electric Field



Quantum Efficiency of Delta-doped detectors

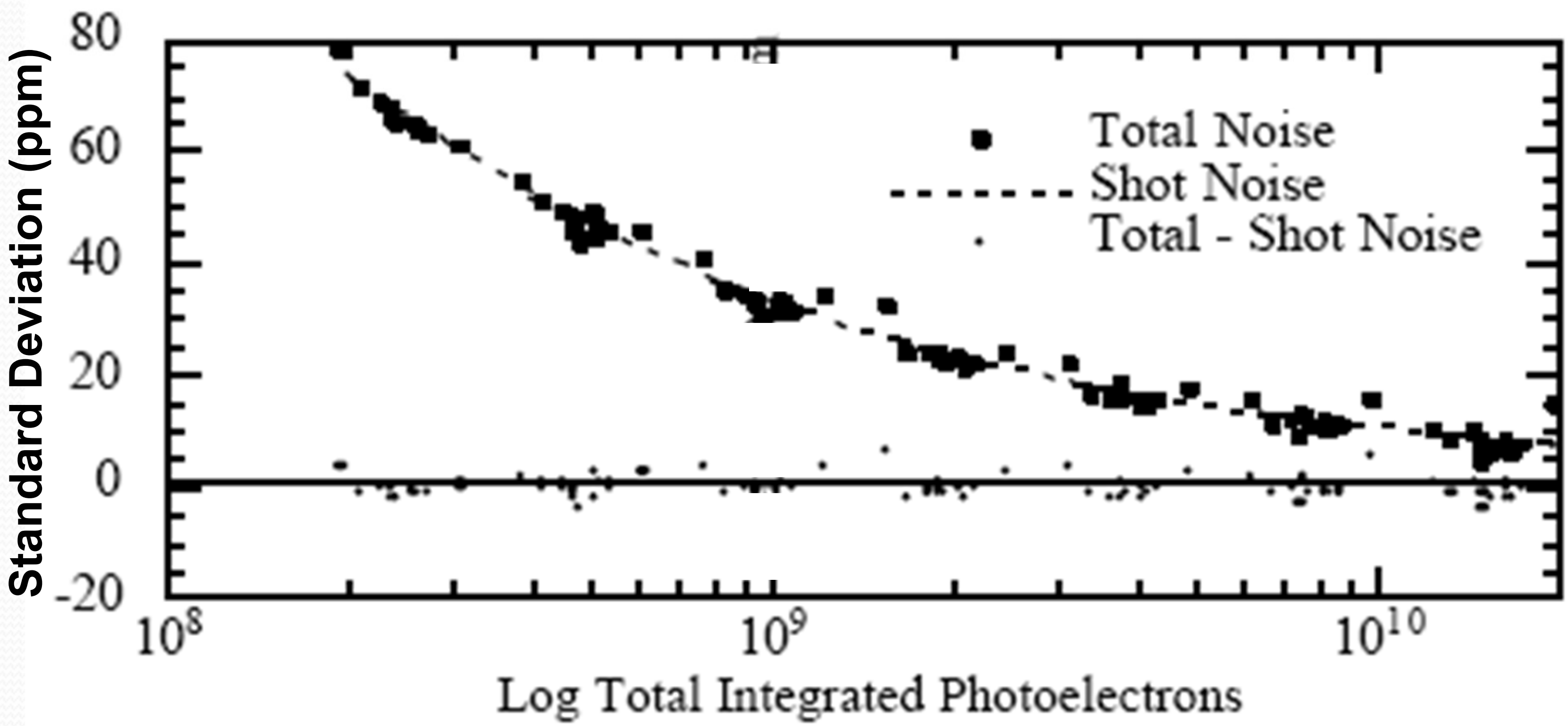




S. Nikzad, "Ultrastable and uniform EUV and UV detectors," *SPIE Proc.*, Vol. 4139, pp. 250-258 (2000).

J. Trauger (PI WF/PC2) – *No measurable hysteresis in delta-doped CCDs*

Photometric Stability of Delta-doped CCDs



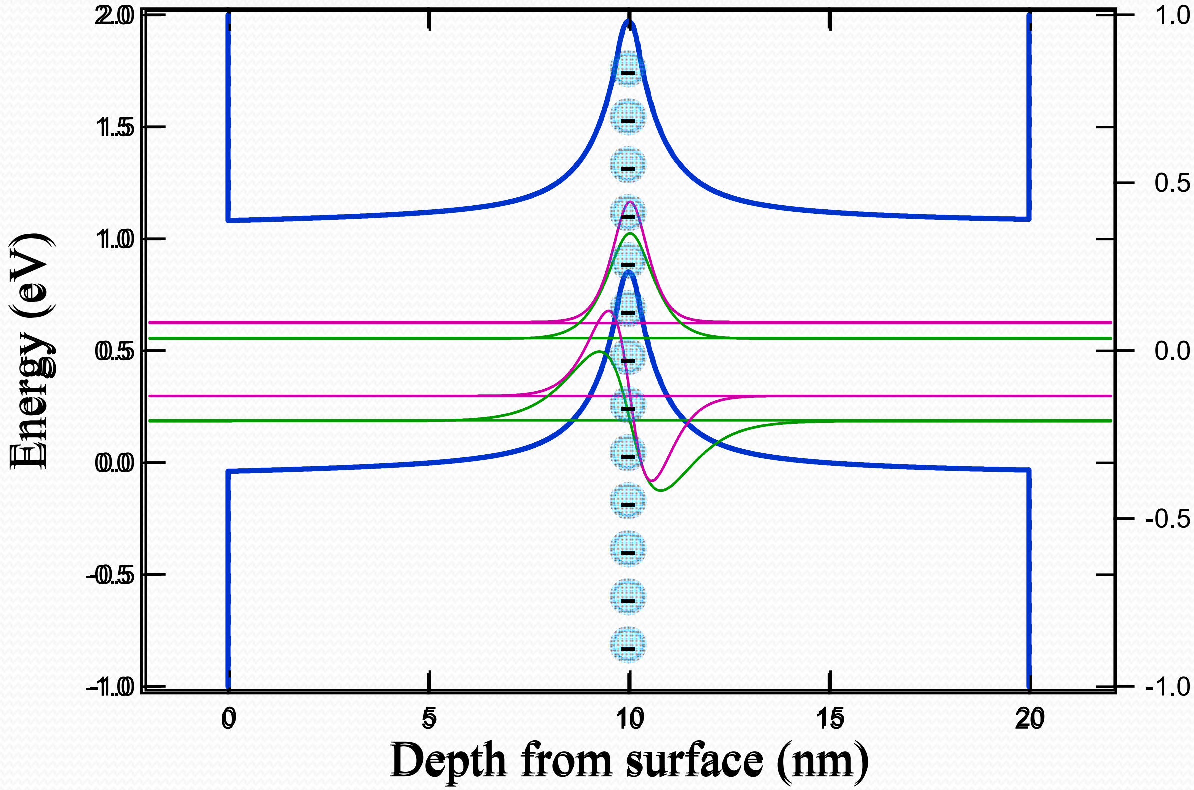
J. M. Jenkins, W. J. Borucki, E. W. Dunham, J. S. McDonald
"High Precision Photometry with Back-Illuminated CCDs,"
ASP Conf Ser ,16-18 Oct. 1996 STScI

…the [delta-doped] CCD performed as a *nearly shot-limited photometer with only a few ppm of error* at an integrated flux of $10^{10}e^-$

The Physics of Delta-doped Silicon

Quantization of states

Delta-doped Silicon

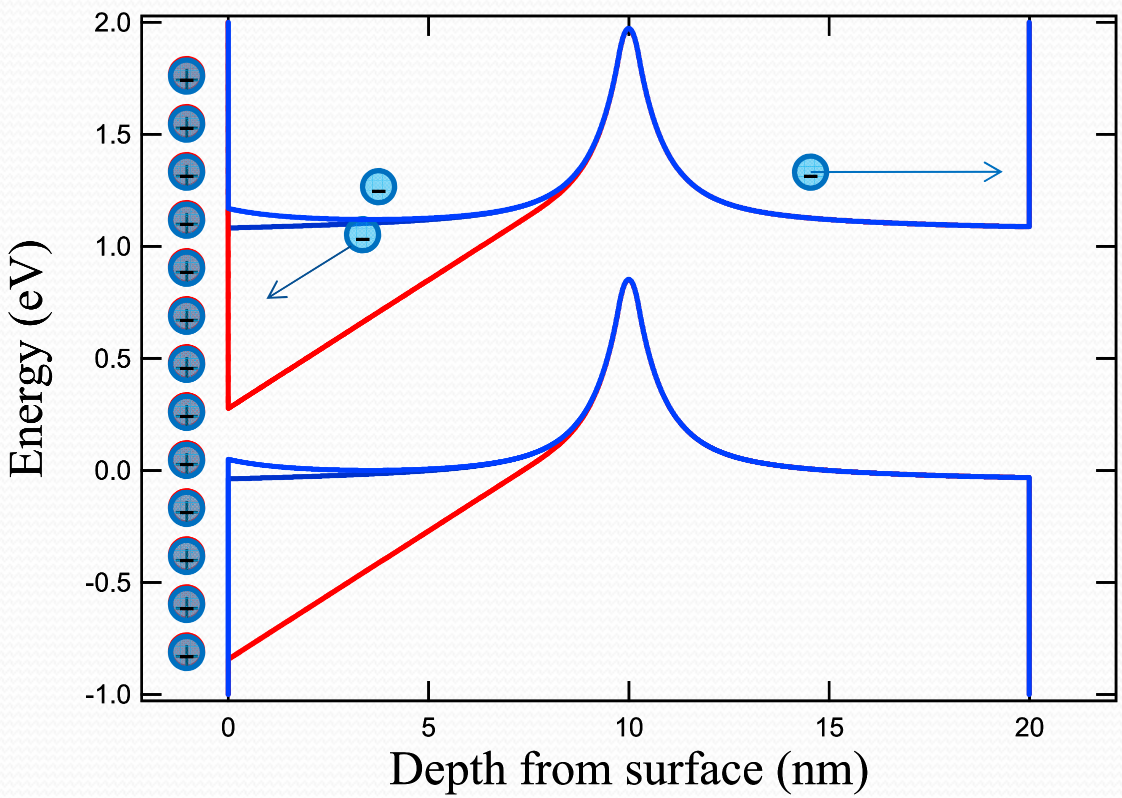


Delta-doping creates “quantum well” in silicon

Majority carriers confined in quantized subbands

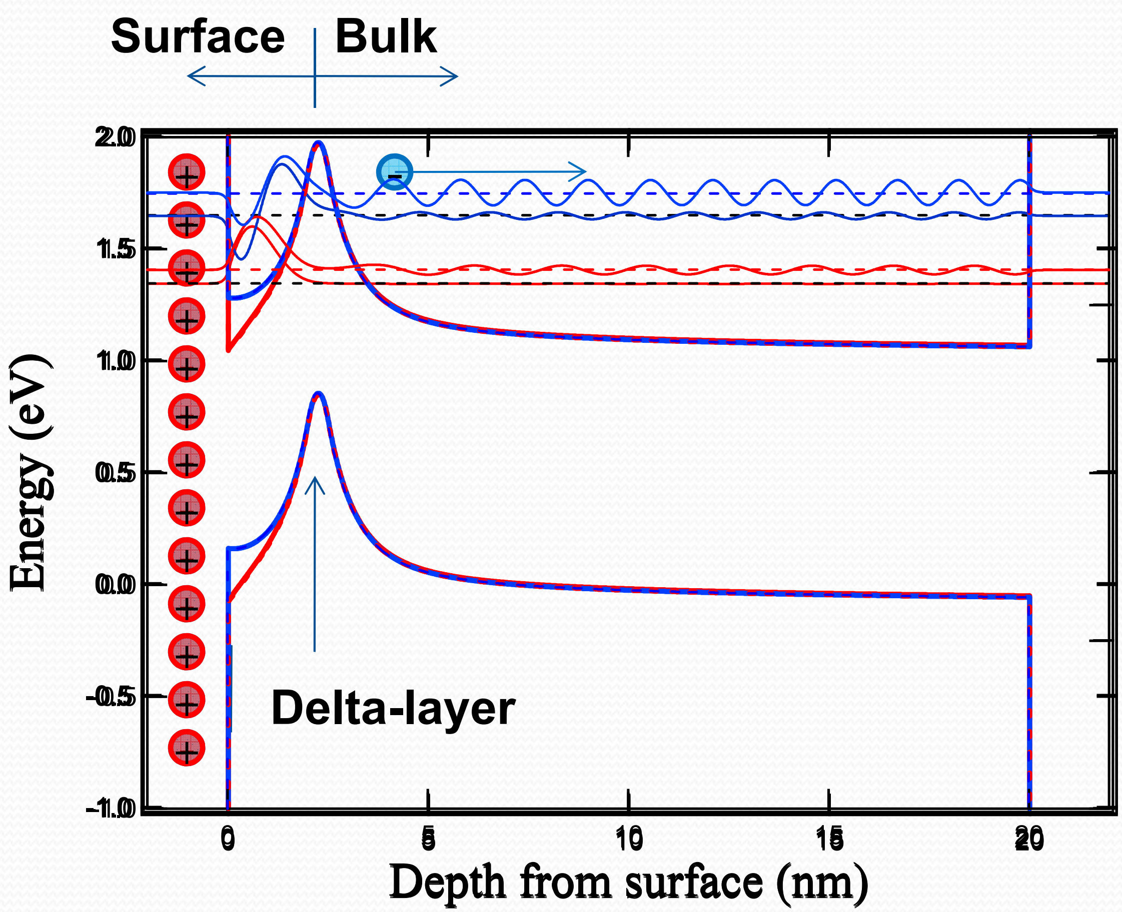
Peak electric field ~10^7 V/cm

Delta-doping and Quasi-isolation



Quasi-isolation → Elimination of QEH

Delta-doping and Quantum Exclusion



Quantum Exclusion → Elimination of trapping

Positively charged surface @ 10^{13} cm^{-2}

The photometric stability of Delta-doped detectors

- **Proven performance**
  - Lyman –alpha flood: No hysteresis! (John Trauger, PI WF/PC 2)
  - Shot-noise limited photometry (Jensen *et al.*, Kepler group)

- **Quasi-isolation**
  - Extroardinarily high fields: 10^7 V/cm
  - Internal fields decoupled from surface charge

- **Quantum exclusion**
  - **Signal (QE):** trapping of minority carriers suppressed by quantum confinement
  - **Noise:** Surface dark current suppressed by delta-layer as tunnel barrier

Chemistry of the Si-SiO_2 interface

The SiO_x Boundary Layer

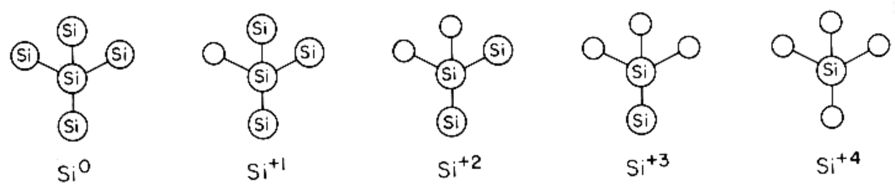


Fig. 35. Illustration of the five possible formal oxidation states for Si.

- Interface is abrupt to 1-2 monolayers
- Local chemistry is difficult to resolve
- Structure is process dependent, including cleaning processes and contaminants
- Strained SiO_2 near the interface is vulnerable to radiation damage
- Radiation breaks Si-O bonds; mobile defects migrate to surface creating amphoteric traps.
- Trapping of holes in near-interfacial region creates fixed positive charge at the interface.

Chemical and electronic structure of the SiO_2/Si interface 121

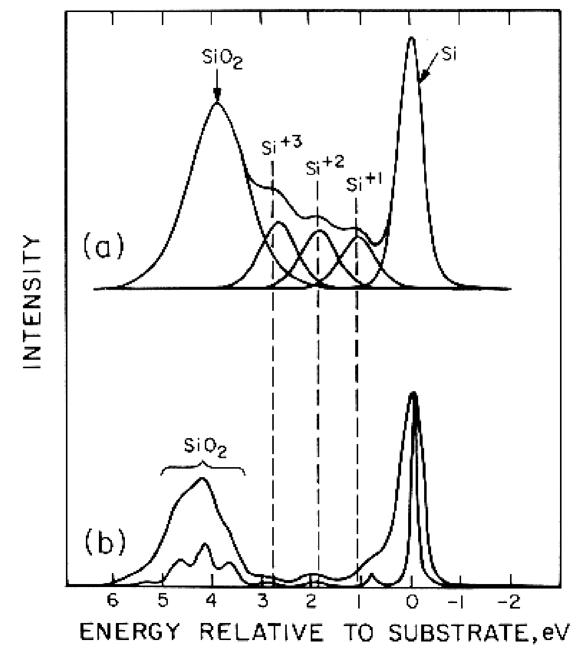


Fig. 36. (a) Si 2p spectrum obtained by Hollinger and Himpsel [144], using synchrotron radiation. The spectral components have been determined by least-squares analysis. The dashed line indicates the position of the Si suboxide states. (b) Mathematical resolution enhancement (bottom curve) of a Si 2p spectrum of thermal SiO_2 grown on Si obtained with Al Kα radiation [62].

F.J. Grunthaner and P.J. Grunthaner,
"Chemical and Electronic Structure of the SiO_2/Si Interface," *Materials Science Reports,*
1 (2, 3): 65-160, 1986.

Si-SiO_2 Interface Geometry

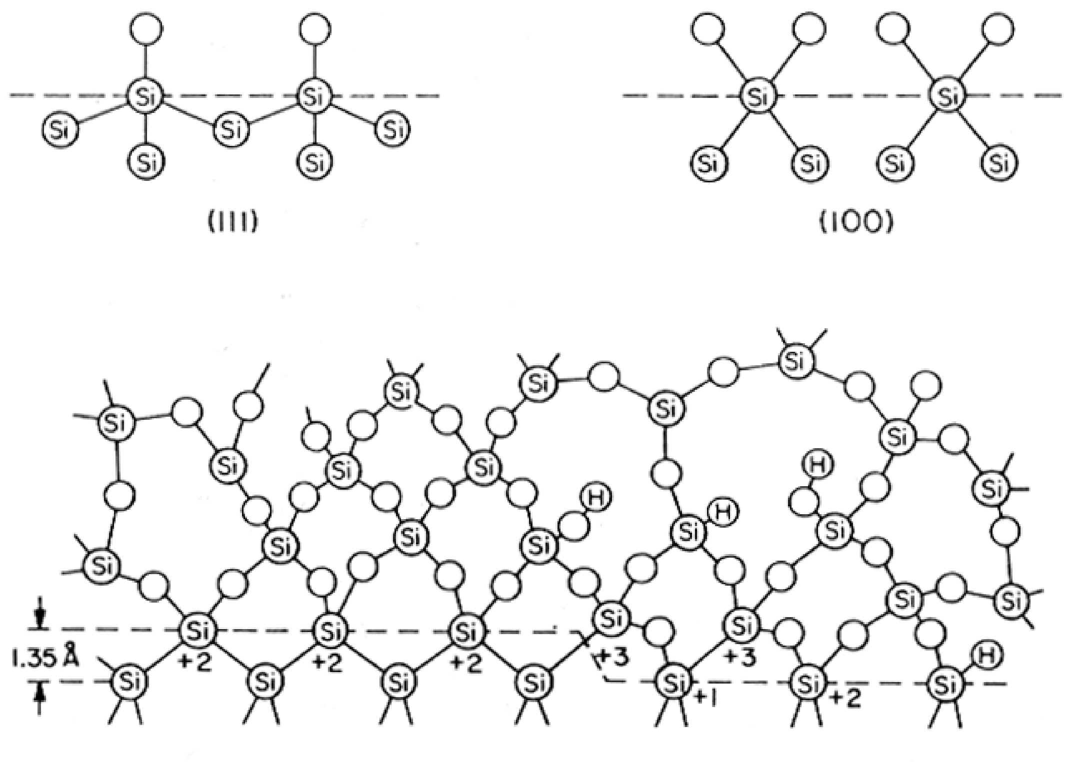


Fig. 41. Idealized diagram of local atomic interface geometry. The upper panel illustrates the suboxide states expected for ideal (111) and (100) surfaces. The lower panel illustrates the inclusion of atomic steps and impurities.

Hydrogen density at the Si-SiO2 Interface

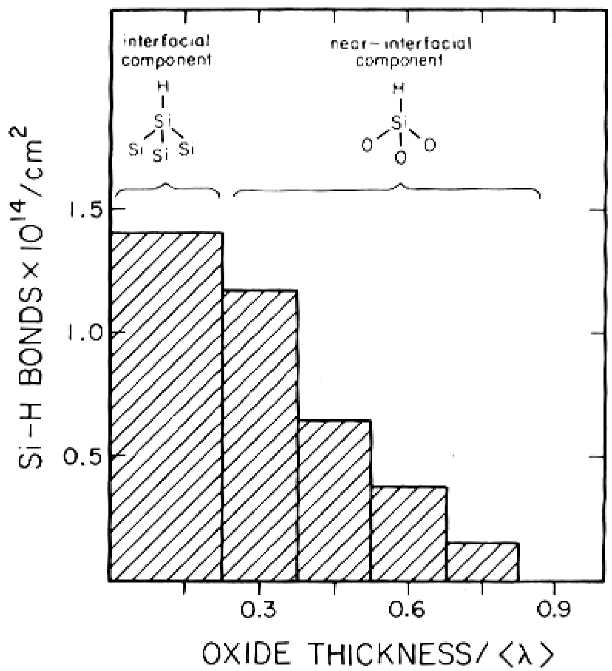


Fig. 58. Histogram of hydrogen concentration as a function of oxide thickness deduced from XPS measurements as discussed in the text.

- XPS data can't differentiate between hydrogen and dangling bonds;
- Interface densities inferred from XPS measurements are on the order of $n_{2D} \sim 1\text{-}2\times10^{14}\,cm^{-2}$

Surface States and Hydrogen

- Surface states
  - P_b centers (Dangling bonds)
    - Estimated density of Si-H at the surface: $n_{2D} \sim 1\text{-}2 \times 10^{14}\ cm^{-2}$
    - Hole trapping can break Si-H bond, and liberate atomic hydrogen from the surface
  - E' centers (Oxygen vacancies in SiO_2)
    - E' center is an electron trap at site of oxygen vacancy
      - Dates to 1950's
      - More than 15 varieties
      - Spectroscopies place defect level at 5.7 – 5.9 eV (~210 nm)
    - Defect is intrinsic to oxygen-deficient silica (not impurity related)
    - Concentrated near Si-SiO_2 interface because SiO_x is oxygen-deficient.
    - E' can catalyze breakup of H_2
    - Hole trapping can convert E' precursor into E' defect and atomic hydrogen, which can in turn react with bridging oxygen to form fixed positive charge at the Si-SiO_2 interface.

Hole traps at Si-SiO_2 Interface

- Hydrogen passivated oxides
  - Hydrogen ties up dangling bonds and eliminates traps
  - Oxide is vulnerable to hot carrier degradation—
    Especially hole trapping!
    - Hole + $O_3{\equiv}SiH \rightarrow O_3{\equiv}Si\cdot + H^+$
    - Hole + $Si_3{\equiv}SiH \rightarrow Si_3{\equiv}Si\cdot + H^+$
- Trapped holes and fixed oxide charge
  - Density of hole traps at Si-SiO_2 interface is sufficient for compensation of a near-surface delta-doped layer.

The Physics and Chemistry of Delta-doped Surfaces

microdevices laboratory

Delta-layer compensation by surface

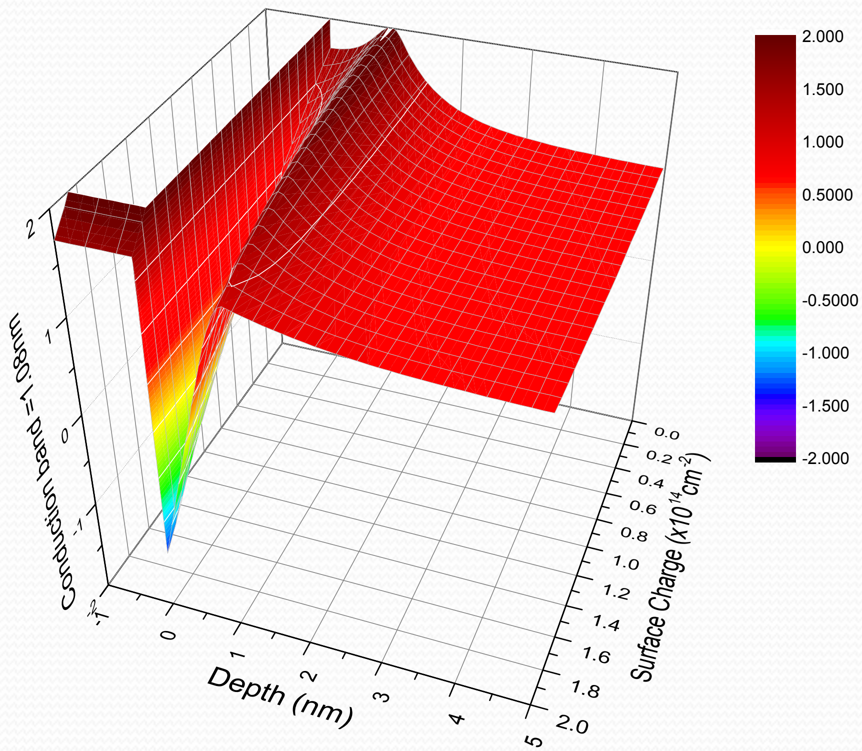
MBE Surface Passivation	Structure	Sheet number ($x\ 10^{14}\ cm^{-2}$)
Delta doping	Shallow (15 A cap layer)	0.05
	Intermediate (25A cap layer)	-0.1 (inversion)
	Deep delta-layer (150A cap layer)	1.2

Hall measurements of sheet number

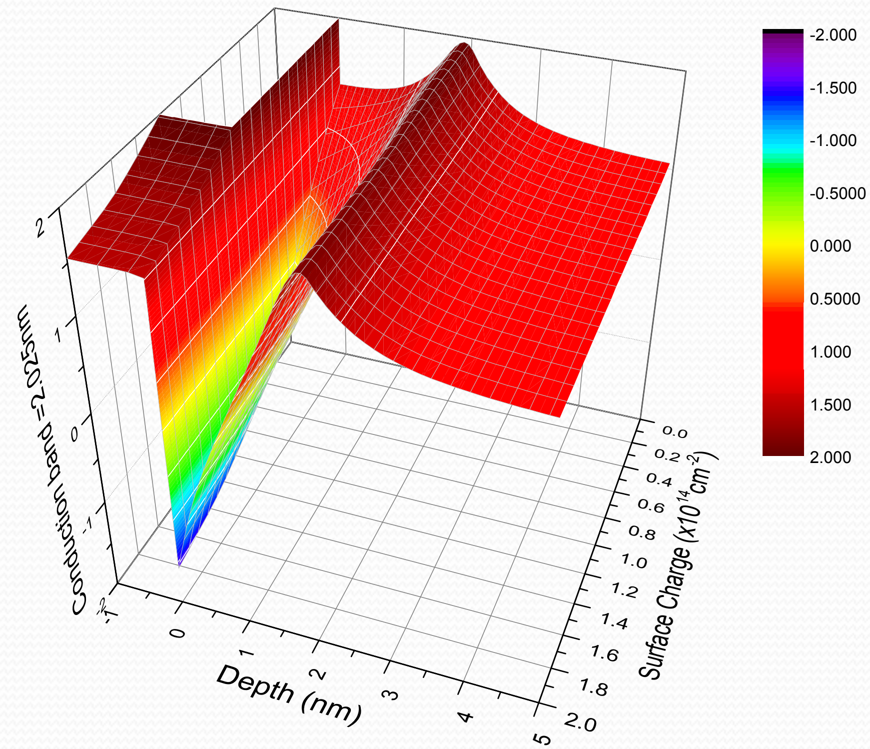
- Comparison of deep and shallow delta-layers demonstrates compensation
- Intermediate cap layer exhibits inversion.

Surface Charge and Quasi-isolation

Conduction Band Edge vs. Surface Charge – Bulk is independent of Surface



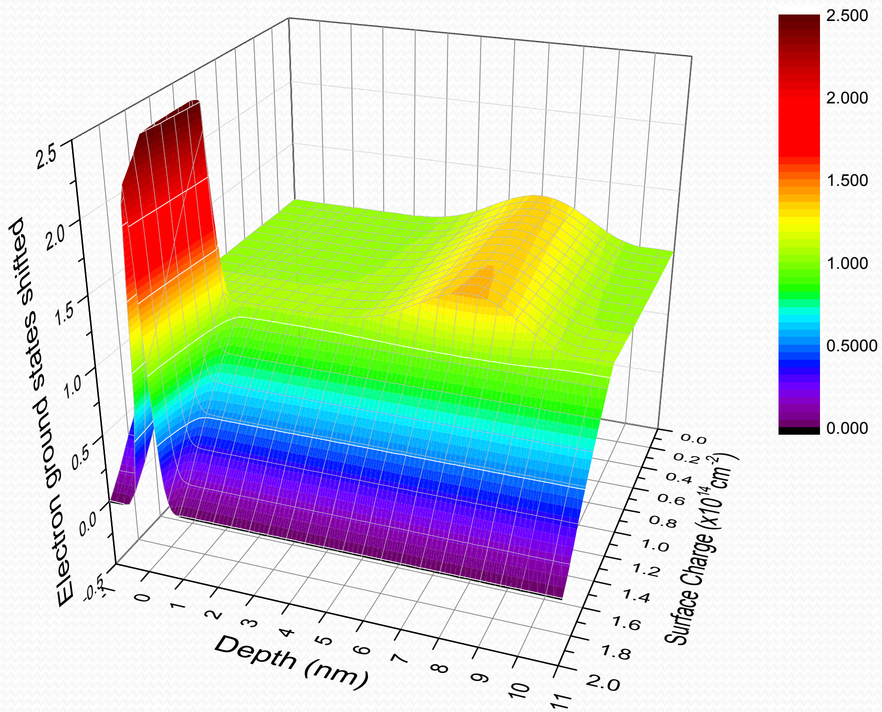
Delta layer depth = 1nm



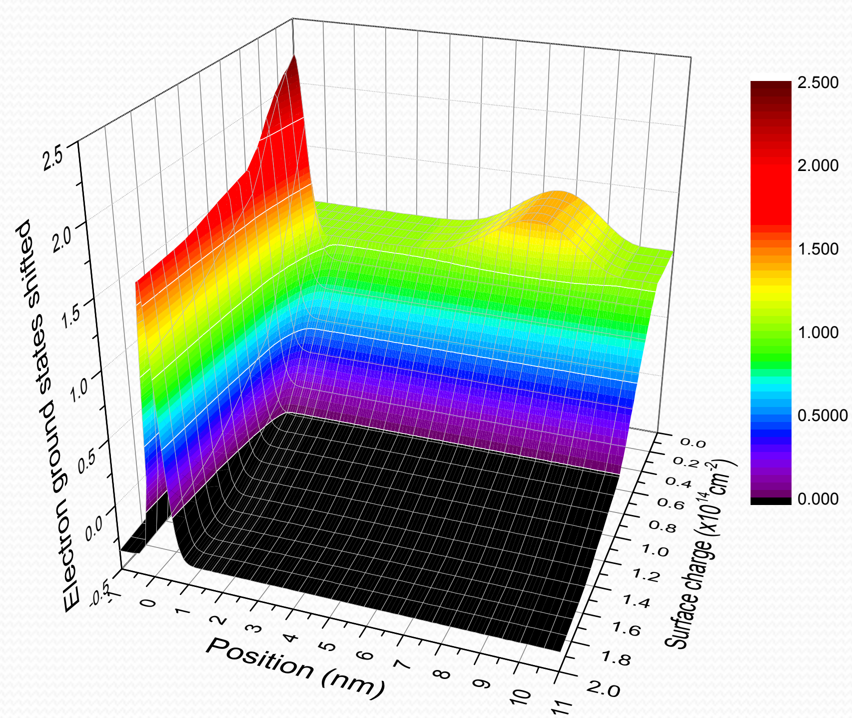
Delta layer depth = 2nm

Tamm-Shockley States

Electron ground states: T-S surface state formation vs. Delta-layer depth

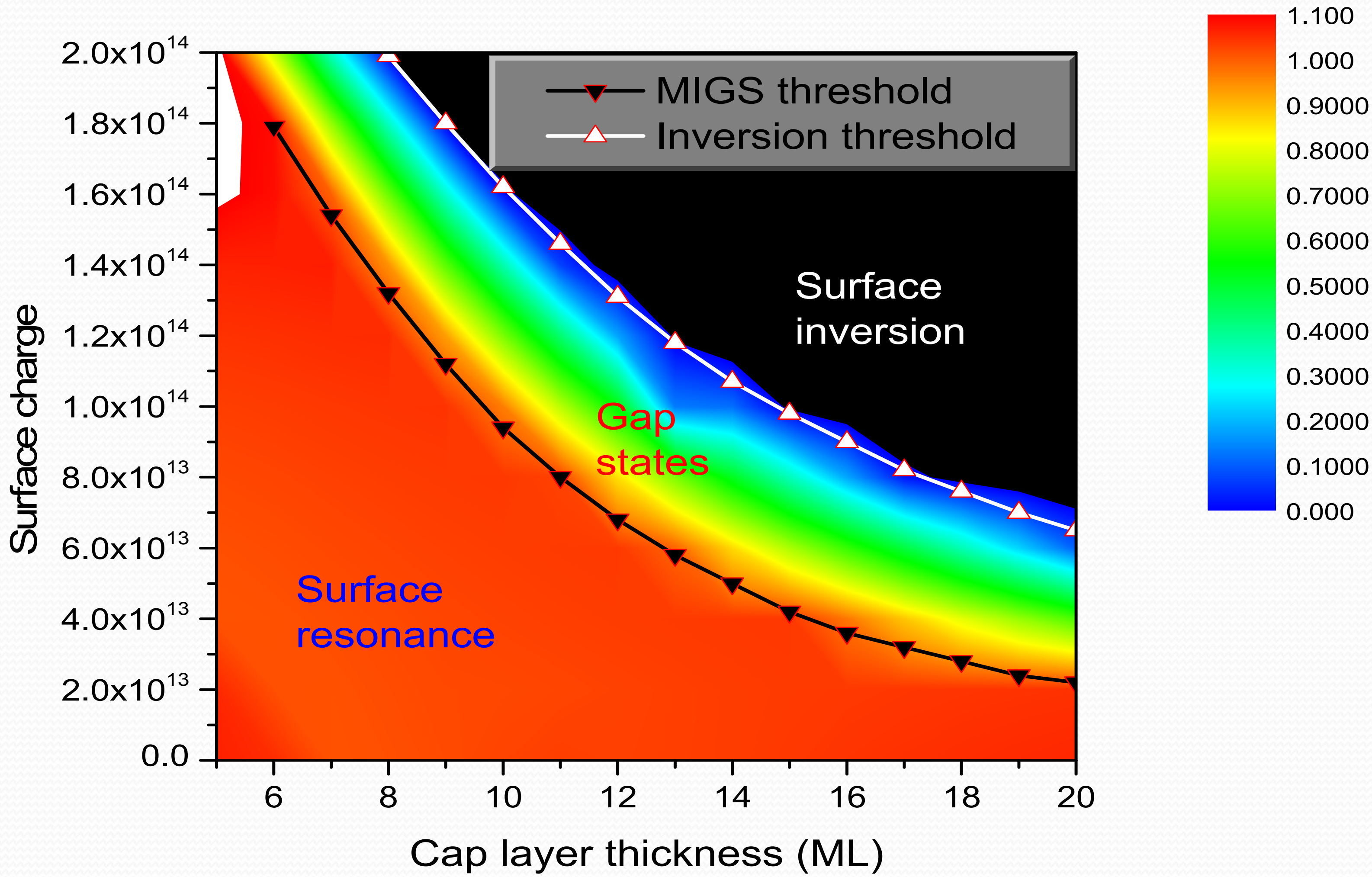


Delta layer depth = 1nm



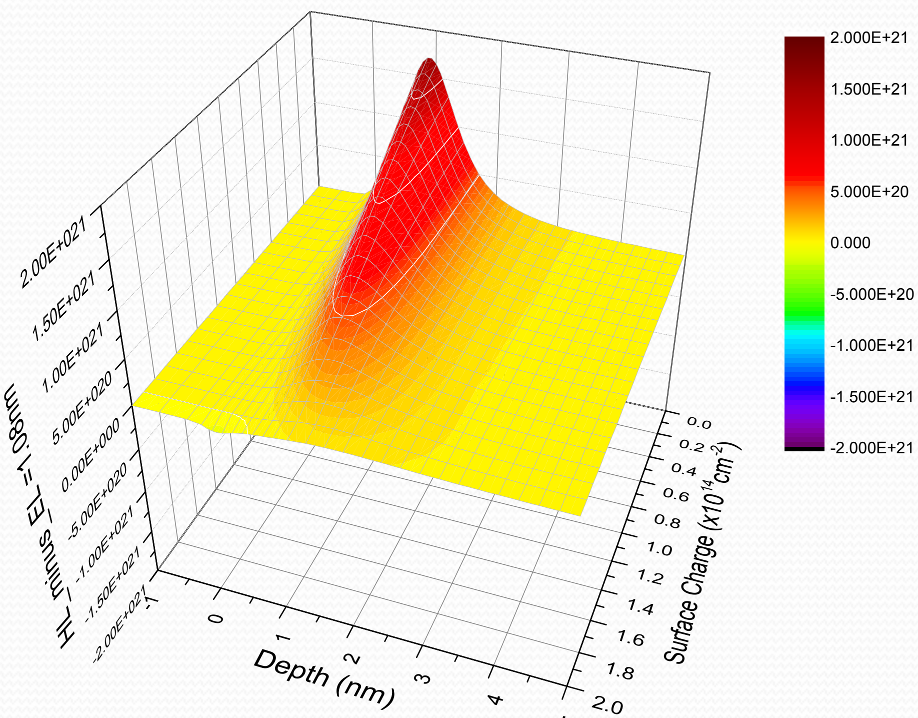
Delta layer depth = 2nm

Surface Passivation by Quantum Exclusion

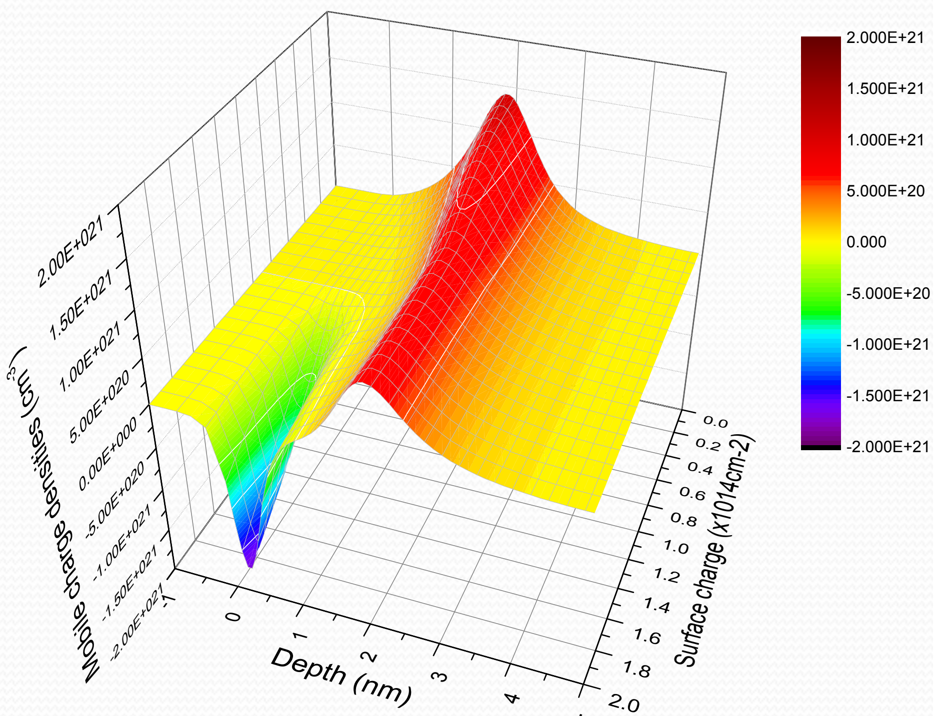


Compensation and Inversion

Distribution of Holes and Electrons vs. Surface charge



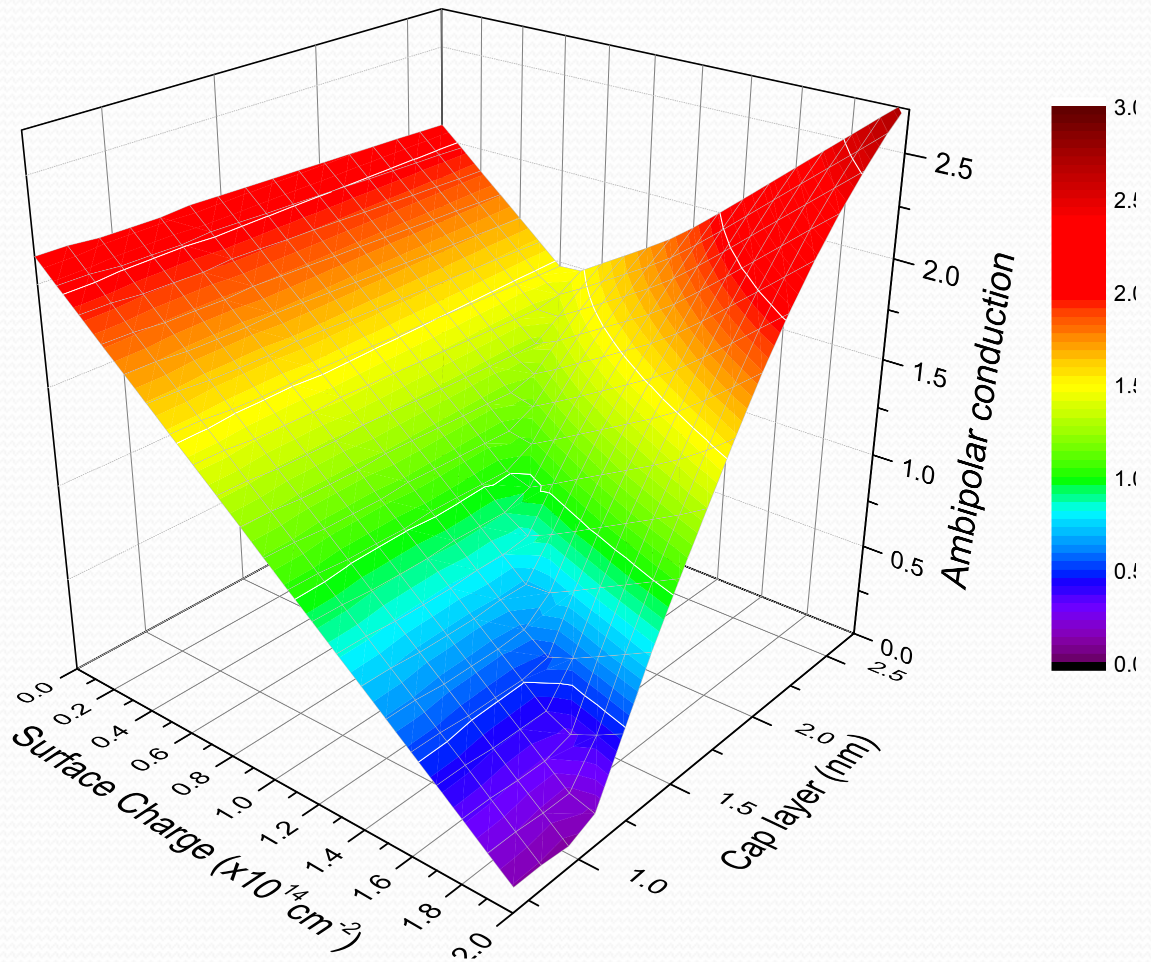
Delta layer depth = 1nm



Delta layer depth = 2nm

Ambipolar Conduction

Integrated sheet densities, holes + electrons



Si-SiO2 Interface

- Compensation of delta-doped surface
  - High quality oxides: $n_{2D} \sim 10^{11}\ \mathrm{cm}^{-2}$
  - Native oxide: $n_{2D} \sim 10^{12} - 10^{13}\ \mathrm{cm}^{-2}$
  - Delta-doped surface: $n_{2D} \sim 1\text{-}2 \times 10^{14}\ \mathrm{cm}^{-2}$

- Hydrogen density at Si-SiO2 interface
  - Silicon atoms on (100) surface: $n_{2D} \sim 7 \times 10^{14}\ \mathrm{cm}^{-2}$
  - Silicon dangling bonds: $n_{2D} \sim 1.4 \times 10^{15}\ \mathrm{cm}^{-2}$
  - Hydrogen density, oxidized surface: $n_{2D} \sim 1\text{-}2 \times 10^{14}\ \mathrm{cm}^{-2}$

Surface compensation at these densities is surprising, but not unreasonable.

Conclusions

1. Quantum confinement of electrons and holes dominates the behavior of delta-doped surfaces
2. Stability of delta-doped detectors: Delta-layer creates a ~1 eV tunnel barrier between bulk and surface
3. At high surface charge densities, Tamm-Shockley states form at the surface
4. Surface passivation by quantum exclusion: Near-surface delta-layer suppresses T-S trapping of minority carriers
5. The Si-SiO2 interface compensates the surface
6. For delta-layers at intermediate depth, surface inversion layer forms
7. Density of Si-SiO2 interface charge can be extremely high ($>10^{14}$ cm^{-2})